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Study on Rheological Behavior of the Composites of Recycled HDPE with Recycled Tire Rubber Particles

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Study on Rheological Behavior of the Composites of Recycled HDPE with Recycled Tire Rubber Particles

(TITLE)

By

Yanze Li

THESIS

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I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
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Abstract:

This study was mainly concerned with rheological properties of composites of recycled high density polyethylene (HDPE) with recycled tire rubber particles at shear rates from 1.167 to 116.7 s^{-1}. The viscosity was investigated in terms of effects of shear rate, shear stress, temperature, concentration of recycled tire rubber particles and heating duration. The temperature was in the range from 160 to 250 °C and the rubber particle concentration was between 0 and 25%. The heat duration for the composites was up to 240 minutes before testing.

The viscosities of composites were decreased with increase in shear rate and shear stress. The change was considerably noticeable when the shear rate was less than 7.5 s^{-1}. Increasing the temperature could also decrease the viscosity of composites of recycled HDPE and recycled tire rubber particles. The effect of temperature was more obvious at lower shear rate. The higher viscosity due to increased content of recycled tire rubber particles was explained in terms of increased interaction between recycled HDPE and recycled tire rubber particles. There was little change in viscosity after recycled HDPE and the composites were held up to 240 minutes at 220 °C.

Acknowledgments

I would like to express my sincerest appreciation and gratitude to Dr. Ping Liu for his direction and support during this research and thesis writing. I would like to thank Dr. Gene Strandberg and Dr. Louis Butler for their advisement and willingness to be my committee members.

This work was performed at the School of Technology at Eastern Illinois University. Financial supports from the Charles A. Lindbergh Foundation, Office of Solid Waste Research of University of Illinois at Urbana-Champaign and Council for Faculty Research are greatly appreciated.

I would like to acknowledge my special appreciation to my wife Li Cai and my son Jiawei Li. Their encouragement, patience, and strength were essential to the success of this research.

Table of Contents

List of Figures

Figure **Page**

CHAPTER 1

Introduction

Polymeric materials play very important roles in the modern society. Polymers such as plastics and elastomers are extensively used in automobile, building construction and packaging industry. As a result of the growing applications, disposal of polymeric products has emerged as a major concern of environmental protection and natural resource conservation.

Plastics occupy a large volume of landfill space quickly being depleted. The US Environmental Protection Agency (1990) estimated that four pounds of trash were generated daily by each person throughout the United States, and that 21% of landfill space was occupied by plastics. Moreover, the number of scrap tires has reached 250 million in the United States. The majority of scrap tires, 78% of total amount of discarded tires, were either landfilled, stockpiled or illegally dumped (Riggle, 1992). Making composites from recycled plastics and rubber is an effective method of cutting product cost, reducing landfill, and fully making use of natural resources.

This research was focused on rheological behavior of composites of recycled high density polyethylene (HDPE) and recycled rubber. The study on rheology of the composite material can help optimize quality of polymeric products. It is hoped that more products can be produced from recycled materials to alleviate the solid waste disposal dilemma due to increasing uses of polymers.

1.1 Statement of the Research

The objective of this proposed research was to study the rheological behavior of composites made of recycled high density polyethylene (HDPE) and recycled tire rubber particles. The composites were produced by extruding a mixture of recycled HDPE and recycled tire rubber particles at various proportions from 0 to 25%. Effects of shear rate, shear stress, rubber content, temperature and holding time at melt temperature will be investigated in terms of changes in viscosity of the composites. Understanding the rheological behavior will not only provide a sound basis for practical processing of the composites of recycled constituents into useful products, but also offer insights regarding materials structure and property change due to recycling.

1.2 Significance of the Research

Information on rheological behavior of composites of recycled HDPE and recycled tire rubber particles can help industry more effectively process the recycled materials into useful products. Different polymer processes require different viscosity of polymers in practical processing. For example, an extrusion molding process needs higher viscosity than injection molding. For the same process, polymers with different viscosity will require different processing parameters such as temperature and pressure. In other words, understanding of rheological behavior will provide a clear guideline for effective processing of composites made of recycled materials.

While industry gains more understanding on rheological behavior of the composites of recycled plastics and recycled rubber, more products can be developed and produced with the recycled materials. This will create an industrial demand for recycled plastics and recycled rubber, which will make recycling an effective and financially viable solution for the solid waste problem.

Recycling efforts by citizens will be promoted technologically. Therefore, more waste materials can be expected to flow into industry instead of landfills. In this way, the solid waste problem affecting our environment can be reduced considerably.

1.3 Definitions

Capillary rheometer -- Instrument for measuring flow properties of polymer melts, using a capillary tube of specified diameter and length. The rheometer can maintain a desired temperature, apply a pressure to force molten polymer through the capillary, and measure differential pressures and flow rates (Cheremisinoff, 1993).

Composite Material -- A material consisting of two or more distinct constituents that have readily discernible interfaces between them.

HDPE (high density polyethylene) -- Polymer consisting of many ethylene monomers. It is usually synthesized from natural gas with some catalysts, under low pressure and at a temperature of 50-70°C. The density of HDPE is in the range of 0.941-0.965 g/cm^3.

Newtonian liquids -- The liquids for which viscosity is independent of shear stress and shear rate.

Pseudoplasticity -- Also called shear thinning. The viscosity decreases as shear rate increases.

Recycled Tire Rubber -- After physically separating metal and polyester cord, the main composition of recycled tire rubber is styrene butadiene, butadiene, natural and butyl rubber, carbon black and some low molecular weight additives.

Rheology -- Study of flow and deformation of materials.

Rheometer -- Instrument that measures the visco-elastic properties of solids, semi-solids

and flow.

Rubber --A material that can be stretched to at least twice its original length and that will retract rapidly and forcibly to its original dimensions upon release of the force.

Shear rate -- Component of the rate of deformation tensor. When a liquid takes laminar flow, one laminar layer is displaced with respect to the adjacent ones by a fraction of the total displacement encountered in the liquid between both plates. The speed drop across the plate thickness is termed shear rate.

Strain -- Change in dimension per unit dimension. In bulk deformation, the strain is the change in volume per unit volume, $\delta V/V$.

Stress -- Force per unit area. In bulk deformation, the stress is the applied pressure, P.

Viscosity -- The resistance of a fluid to any irreversible positional change of its volume elements. Viscosity can be expressed in a ratio of stress to strain rate with a unit Ns/m^2 (Pa s) in SI system.

1.4 Assumptions

The following assumptions were made for the research.

(1) Difference in loading time for different samples was not significant in affecting viscosity.

(2) Thermal conductivity of the composite was constant within the range of test temperature.

(3) Frictional heat generated during tests was not considered.

(4) The entrance loss for viscosity measurement was not corrected.

1.5 Limitations

In this research, several parameters were limited as following:

1. The compositions of recycled HDPE and recycled tire rubber were determined by the suppliers. Impurities in recycled HDPE and recycled tire particles are unknown.

2. The processing of the composites was out of the scope of the research.

3. Instrument errors such as temperature and shear stress was determined by the testing equipment.

1.6 Delimitations

The factors controlled in this research are listed as following:

1. The percentage of recycled rubber was selected 5, 10, 15, 20 and 25 by weight in the composite, respectively.

2. The temperature was set in the range from 160 to 250 °C

3. The range of apparent shear rate was chosen from 1.167 to 116.7 s^{-1}.

1.7 Hypotheses

The hypotheses in the research were:

(1) With the increase of temperature, the viscosity of the composite will decrease.

(2) The viscosity of the composite will increase as the percentage of recycled rubber increases.

CHAPTER 2

Literature Review

Polyethylene is the largest volume plastic in industry. Its discovery in the 1930s was one of the landmarks of plastics industry. A wide variety of types and grades of polyethylenes are available commercially, which share characteristics such as low price, chemical inertness, good electrical properties, and easy processing. Density remains a good indicator of the general level of crystallinity, which affects many properties, such as stiffness, resistance to permeation by gases and resistance to oils and greases. Those properties generally increase with increase of density. High density polyethylene is associated with the more rigid polyethylene with a density in the range 0.941-0.965 g/cm^3 (Charrier, 1991).

Polyethylene grades are also classified according to their melt viscosity or melt index, which strongly reflects the molecular weight of the polymer. This is of particular importance for processing where different techniques often call for different melt viscosities. Injection molding, for example, is generally associated with an easy flowing grade, while thermoforming requires a high melt "consistency" or viscosity.

Rubber is usually classified into two major kinds -- natural and synthetic rubber. Tire rubber is typically made from polybutadiene styrene-butadiene (SBR), natural rubber (NR), polyisoprene synthetic rubber (IR), butyl rubber (IIR), ethylene-propylene-diene (EPDM) (Kroschwitz, 1989).

Rheology, the science of deformation and flow of materials, provides necessary knowledge for processing plastics into products. Liquid-like materials in many industrial processes cover a wide range of flow behavior. Satisfactory operation of these processes requires

a knowledge of the material's flow properties under operational conditions. Thus understanding rheological behavior of the materials can help in the design of improved process technology. Moreover, rheological behavior of polymer melts will also affect the ultimate material properties of products.

Rheometry is the art of measuring deformation and flow properties of materials (Cogswell, 1981). There are five methods of measuring rheological behavior: rotational, squeezing, extrusion, torque, and free surface flows (Schramm, 1994). Capillary flow is one of the methods of extrusion type.

Capillary tube viscometer is one of the simplest and most widely used instruments for rheological characterization. A plunger, extruder, or other pressure source drives the sample through a slit capillary at either constant or programmed flow rate. When using slit capillaries, one can measure the pressure difference directly in the capillary. But this limits the shear rate range to values rarely exceeding 1000 s^{-1}. Capillary rheometry has found its main area of application in the measurement of polymer melt viscosities at shear rates below 1000 s^{-1} and at temperatures up to 500 °C. There are many advantages in using capillary rheometers. These include the relative ease of filling, the ability to change temperatures and shear rates readily, the similarity in shear rates and flow geometry to those actually found in extrusion, the ability to detect some indication of polymer elasticity, and the ability to study the surface texture of the extrudate. The main disadvantage of the technique is that shear rate varies across the capillary, and that corrections are needed in order to obtain accurate viscosity values.

No same studies as this research have been found in the literatures. Several studies which deal with similar materials or method of study are summarized as following.

Vadhar and Kyu (1987) reported very detailed information on effects of mixing on morphology, rheology, and mechanical properties of blends of ultra-high molecular weight polyethylene (UHMWPE) with linear low-density polyethylene (LLDPE). Rheological and mechanical properties of these blends were profoundly affected by the mixing techniques and rheological results showed yield characteristics of UHMWPE/LLDPE blends, in particular in blends of high UHMWPE contents. Tensile properties of sequentially loaded blends vary more or less linearly with blend compositions. As to the 20/80 blend of UHMWPE/LLDPE, the apparent viscosity monotonically increased with decreasing apparent shear rate at a temperature range from 180 to 250 °C. Considering the end effect and Rabinnowitsch correction, the corrected viscosity of LLDPE increased gradually with decreasing shear rate. However, as UHMWPE component was added, the magnitude of viscosity at given shear rate increased significantly.

Duck and Milner (1967) studied the blending of low *cis* polybutadiene with polyethylene. It was reported that polybutadiene could be used to improve the impact strength of polyethylene, particularly of the sheet grade used for containers and sacks. The improvement in this property allowed for a polyethylene sack to compare favorably in strength and price with the five-ply paper sacks widely used for such materials as cement and fertilizers. Compared to unmodified polyethylene, the impact strength of polyethylene with 10% polybutadiene increased from 0.37 to 0.97 m/kg (falling dart method). In addition, the viscosity of the blend increased with addition of polyethylene at 100 °C.

Roy, Bhattacharya and Gupta (1993) did a rheological study on thermoplastic elastomeric blends of natural rubber and high density polyethylene with varying amounts of carbon fibers. The study only reported the rheological property of composite containing 30 percent HDPE and 70

percent natural rubber and that of the composite filled with carbon fibers. The experiment was done at four different apparent wall shear rates (50.6, 101.2, 202.4, and 401.2 s^{-1}) and three temperatures (160, 180 and 200 °C). The rheological results showed that the composites behaved as pseudoplastic materials. The viscosity decreased with increasing shear rate at all temperatures and fiber loading, and at a particular shear rate the viscosity of the system fell with increased temperature.

Wang and Fu (1990) studied the relationship between structure, properties, and composition of HDPE/NBR blends as well as interaction between HDPE and NBR. The results demonstrated that a small amount of acrylonitrile-butadiene rubber (NBR) can obviously improve the impact strength, elongation and environmental stress crack resistance (ESCR). A possible mechanism was proposed that repulsion effects between polyacrylonitrile and polybutadiene on segments of NBR caused a local diffusion of butadiene fragments into HDPE phase, forming oriented acrylonitrile microblocks on the interface. On the other hand, NBR might be slightly crossed while blending which enforced the adhesion between HDPE and NBR phase.

George, Joseph, Thomas, and Varughese (1995) studied the HDPE/NBR blend. They mainly focused on the morphology, mechanical properties and compatibilization. As to morphology, it was clear that NBR existed as large domains in HDPE matrix. Increasing NBR content resulted in decreasing Young's modulus, yield stress, tensile strength. It was believed that after adding NBR the crystallinity of the blend was reduced. Moreover, the degree of drop was proportional to contents of rubber. Maleic-modified polyethylene (MAPE) and phenolic-modified polyethylene (PhPE) could be used as compatibilizing agents for HDPE/NBR blends. Data from this study indicated that 5% MAPE and 8% PhPE were enough to produce saturation

at the interface. By the addition of those compatibilizers, the dispersed phase size between HDPE and NBR could become reduced and particles size distribution would become more uniform. Thus, mechanical properties of the blends were substantially improved.

Rajalingam and Baker (1992) studied the role of functional polymers in ground rubber tire (GRT) polyethylene composites. The composition of ground rubber tire in their study was 40-50 wt.% rubber (styrene-butadiene, butadiene, natural, and butyl rubber), 25-40 wt.% carbon black and 1-15 wt.% additives. Adding functional polymers into polyethylene increased impact energy of the composites. Major drop in impact energy was observed after GRT was added, but adding functional polymers reduced much of impact energy drop. They concluded that the increase in the impact energy obtained with the styrene block copolymers was due to toughening of the polyethylene matrix, whereas the reactive functional polymers acted as mild coupling agents at the polyethylene-GRT interface. The particle size of GRT could also influence the impact energy of the polyethylene-GRT composite. Smaller particle size of GRT led to higher increase in impact energy.

Pramanik and Dickson (1995) investigated thermoplastic compounds from waste plastics and ground rubber tires. The compounds were prepared by incorporating ground rubber tire (10-40%) into various waste plastics. Polymeric compatibilizer was used to improve the compatibility between the plastic matrix and ground rubber. The melt flow index (MFI) and most tensile and flexural properties were decreased with the increase in ground rubber tire loaded into the waste plastics. The improvement in impact strength of the compounds was explained in terms of increased ductility of the compounds by ground rubber tire, coupling action of compatibilizer at the plastic/rubber interface and /or the plastic matrix toughening.

CHAPTER 3

Methodology

3.1 Materials

The materials used in this research were recycled high density polyethylene (HDPE) and recycled ground tire rubber. The recycled HDPE in pellet form was provided by Quantum Chemical Co. The recycled rubber particles, from 40 mesh (0.425 mm) to dust, were supplied by Aztech Industries, Springfield, Illinois. The composites were made by extruding a mixture of recycled HDPE and recycled rubber particles at various proportions. Six different percentages of recycled rubber particles (0, 5, 10, 15, 20 and 25% in weight) were used in experiments.

3.2 Experimental Details

A capillary rheometer, INSTRON Rheopack, was used for this study. The testing system consists of a main loading frame with controlled displacement rate. The machine offers the capability of controlling shear rate for polymeric composites under compression. The testing frame is controlled by a microcomputer using a software, Rheosoft, which can manipulate the cross head movement according to the established velocity schedule. The system measures the resistance or load to press the polymeric melt through a capillary die, corresponding to the shear rate. Apparent shear rate, shear stress and viscosity are recorded while corrected shear rate, shear stress and corrected viscosity are calculated using Rabinowitsch correction. All the data are recorded in a report data file.

To investigate the effect of shear rate on the viscosity of the composites, shear rate was varied from 1.167 to 116.7 s^{-1}. This was achieved by setting up a velocity schedule for the plunger movement controlled by the microcomputer. The percentage of recycled rubber varied

from 0 to 25% with an increment of 5% to study the effect of rubber concentration on the viscosity of the composites. To understand the effect of temperature on the viscosity of the composites, temperature was set at 160, 180, 200, 220, and 250 °C. Moreover, polymers may be exposed to different heat history during recycling and reprocessing. The heat history can be simulated by varying length of time a composite is heated. In this experiment, the duration at certain temperature was 30, 60, 120 and 240 minutes. The effect of heat duration was designed to provide some insights on the structural change in the polymer caused by recycling. Table 1 lists all the three major experiments for this study.

	Experiment 1	Experiment 2	Experiment 3
Purpose	Study the effect of rubber content	Study the effect of temperature	Study the effect of heating duration
Rubber concentration (wt.%)	0, 5, 10, 15, 20 and 25%	0, 5, 10, 15, 20 and 25% for each temperature	0, 5, 10, 15, 20 and 25%
Temperature (°C)	160, 180, 200, 220, and 250 °C for each composition	160, 180, 200, 220, and 250 °C	220 °C
Shear rate (s^{-1})	Vary from 1.67 to 29.18	Vary from 1.167 to 29.18	Vary from 1.167 to 116.7
Heating time before test (min)	The same	The same	30, 60, 120, and 240

3.3 Data Analysis (INSTRON, 1991)

Viscosity is defined as the ratio of shear stress to shear rate. In a capillary rheometer the wall shear stress is given by

$$\tau_w = \frac{\Delta p}{2l_c} r \qquad (1)$$

where Δp is the pressure drop across the length, l_c, of the capillary tube.

The wall shear stress can be expressed as

$$\tau_w = \frac{\Delta p}{4} \frac{d_c}{l_c} \qquad (2)$$

where d_c is the capillary diameter.

The force, F, acting on the plunger, measured by a load cell, is

$$F = A_p \Delta p \qquad (3)$$

where A_p is the cross-sectional area of the plunger. Thus, the wall shear stress is

$$\tau_w = \frac{F}{4A_p \frac{l_c}{d_c}} \qquad (4)$$

For Newtonian liquids, since the velocity profile is parabolic, shear rate $\dot{\gamma}$ (or velocity gradient) at the wall is

$$\dot{\gamma}_w = \frac{8V}{d_c} \qquad (5)$$

where V is the mean velocity of the liquid flowing through the capillary. The mean velocity is readily calculated from the plunger speed and the ratio of barrel diameter, d_b, to capillary diameter, d_c:

$$V = \frac{V_p}{60} \left(\frac{d_b}{d_c}\right)^2 \qquad (6)$$

where V_p is the plunger speed. Thus, the shear rate in reciprocal second is

$$\dot{\gamma} = \frac{2}{15} V_p \left(\frac{d_b^2}{d_c^3}\right) \tag{7}$$

From the shear rate and shear stress as determined above, the apparent viscosity, η_a, can be determined by

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \tag{8}$$

In the case of non-Newtonian fluids, the velocity profile deviates from parabolic form depending on the degree of non-Newtonian behavior. This means that wall shear rate will be different from that given above for a Newtonian liquid. The Newtonian value $8V/d_c$ is often called apparent wall shear rate. Corrected wall shear rate may be found using Rabinowitsch correction:

$$\dot{\gamma}_c = \frac{3n+1}{4n} \frac{8V}{d_c} \tag{9}$$

where

$$n = \frac{d\ln\tau_w}{d\ln\left(\frac{8V}{d_c}\right)} \tag{10}$$

The value of n is the slope of the graph of $\ln \tau_w$ versus $\ln (8V/ d_c)$.

The wall shear rate for a non-Newtonian fluid is, therefore,

$$\dot{\gamma}_c = \frac{2}{15} \frac{3n+1}{4n} V_p \frac{d_b^2}{d_c^3} \tag{11}$$

The corrected viscosity of the fluid, $\eta_{c,}$ can then be established from the same expression

as equation (8).

$$\eta_c = \frac{\tau_w}{\dot{\gamma}_c} \qquad (12)$$

After each test, there was a report produced by Instron rheology software. The report provides data including plunger velocity, shear rate, final load, shear stress, apparent viscosity, remaining barrel, corrected shear rate, corrected viscosity, calculated shear stress, difference between calculated and experimental shear stress.

CHAPTER 4

Results and Discussion

4.1 Effect of Shear Rate

Figure 1 shows the variation of corrected viscosity of recycled HDPE with corrected shear rate at various temperatures. It is noted that the viscosity of recycled HDPE decreased with increasing shear rate. The rate of decrease was much more drastic at lower shear rate. After the shear rate exceeded 7.5 s^{-1}, the rate of decrease was slowed down significantly. This variation pattern in viscosity with shear rate indicated that the range of shear rate chosen for this study was effective to show the rheological behavior of recycled HDPE.

Figure 2 through Figure 6 depict the viscosity as a function of shear rate for composites of recycled HDPE with recycled tire rubber content of 5, 10, 15, 20 and 25 percent, respectively. For all the composites with different rubber concentration, the viscosity decreased with increasing shear rate. As in the recycled HDPE shown in Figure 1, the rate of viscosity decrease with shear rate was more significant at a shear rate lower than 7.5 s^{-1}. It is also noted that as the rubber concentration increased, the rate of decrease in viscosity in the range of lower shear rate was increased.

It is noted that the composites are pseudoplastic fluid because all the plots have the same characteristic that viscosity decreased when shear rate increased. Moreover, it is easily realized that when shear rate is higher than 35 s^{-1} near Newtonian behavior can be observed.

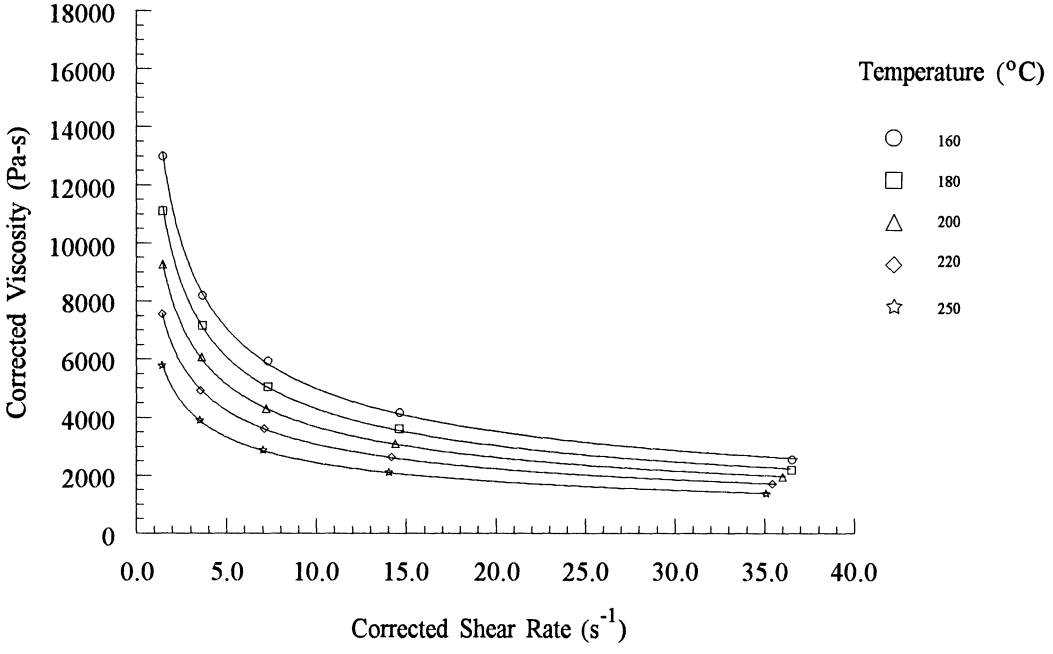

Figure 1. Effect of corrected shear rate on corrected viscosity of recycled HDPE.

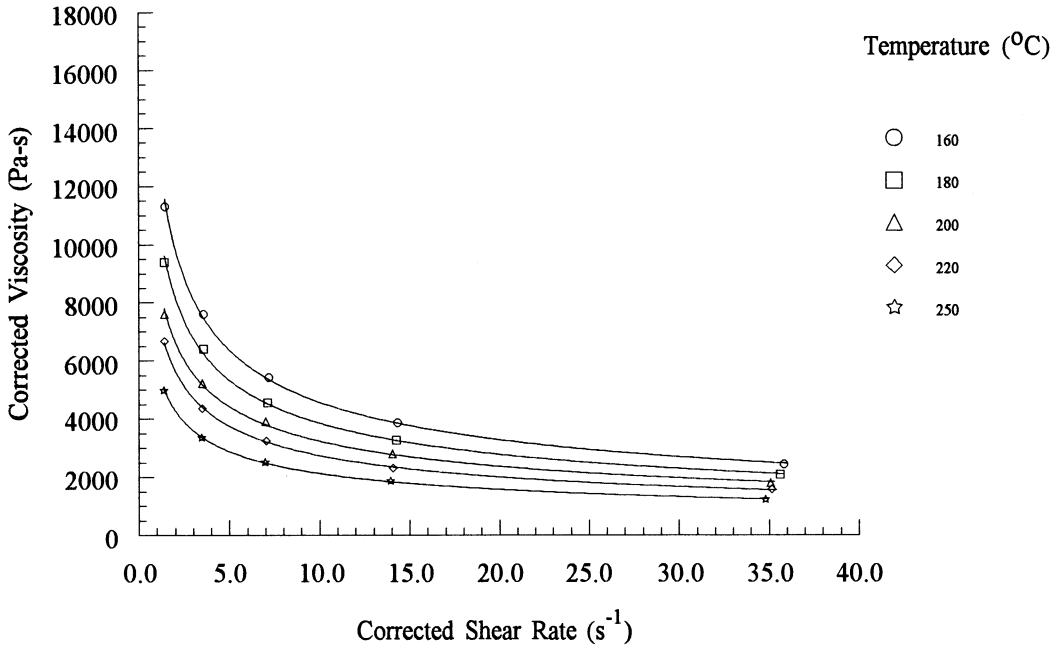

Figure 2. Effect of corrected shear rate on corrected viscosity of the composite of recycled HDPE with 5% recycled tire rubber particles at five different temperatures.

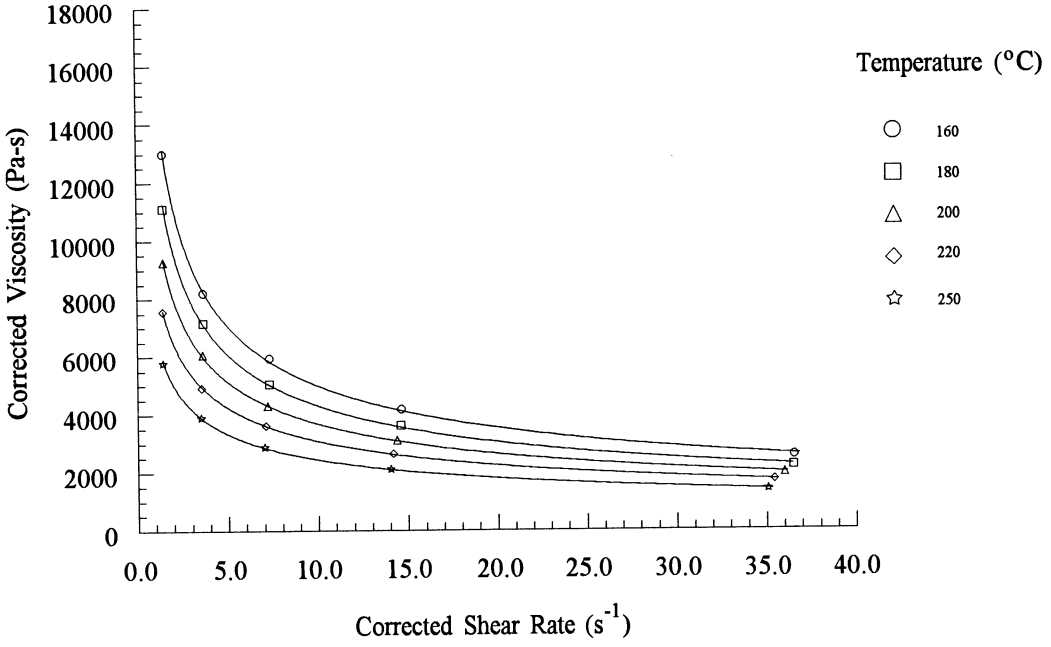

Figure 3. Effect of corrected shear rate on corrected viscosity of the composite of recycled HDPE with 10% recycled tire rubber particles at five different temperatures.

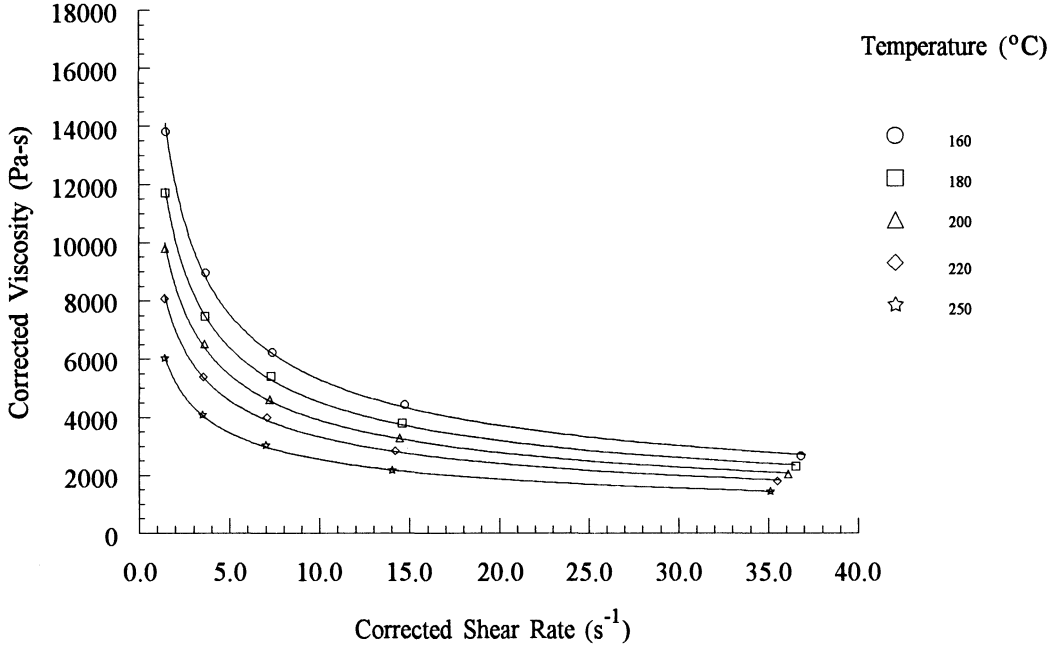

Figure 4. Effect of corrected shear rate on corrected viscosity of the composite of recycled HDPE with 15% recycled tire rubber particles at five different temperatures.

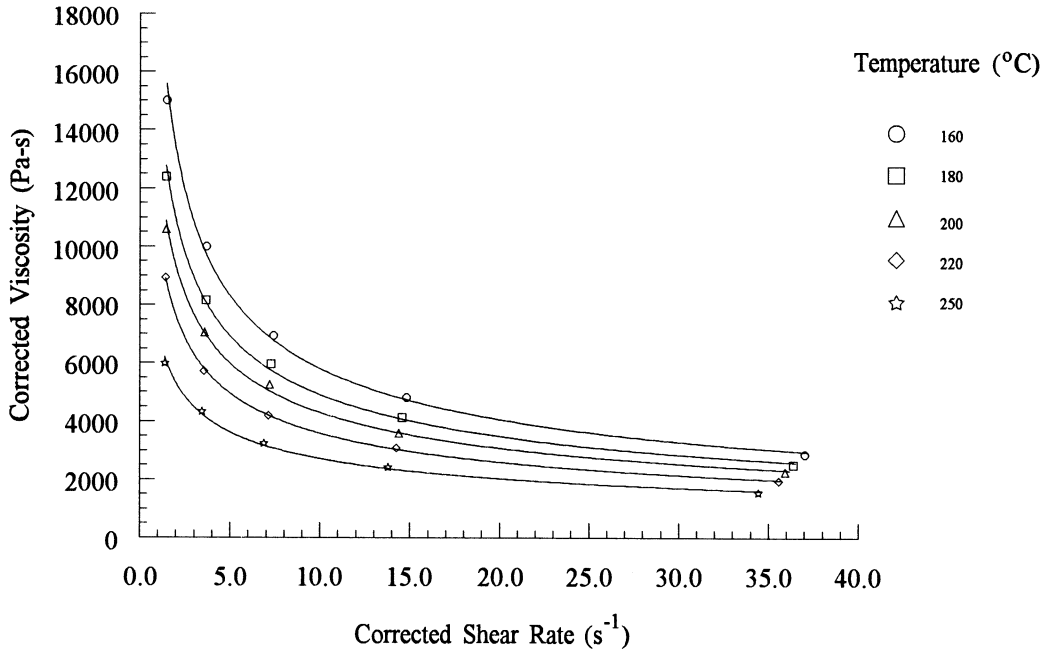

Figure 5. Effect of corrected shear rate on corrected viscosity of the composite of recycled HDPE with 20% recycled tire rubber particles at five different temperatures.

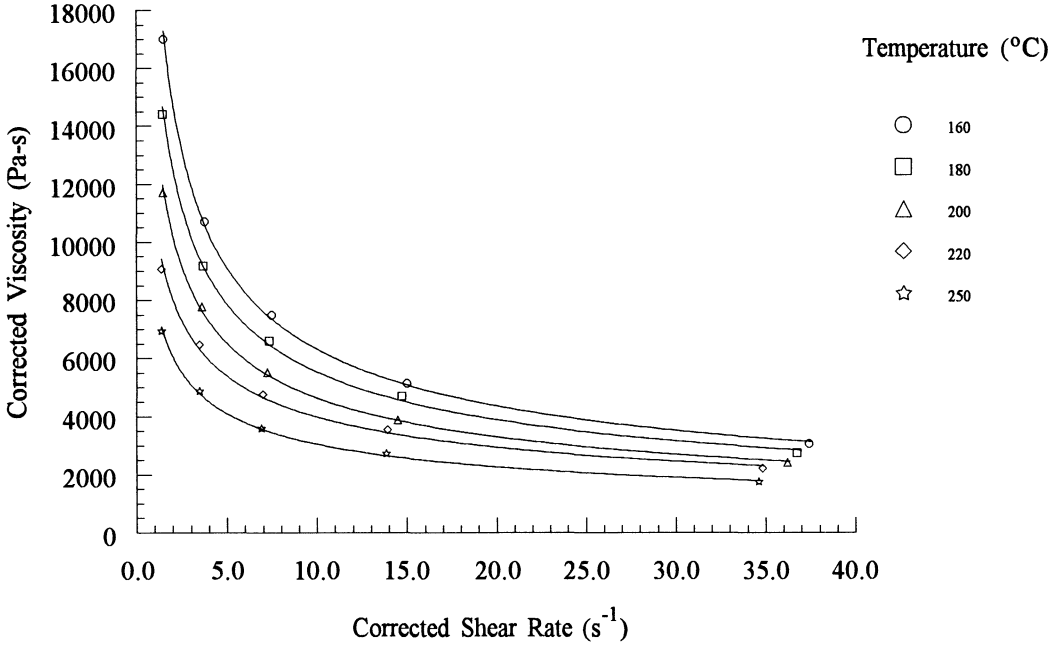

Figure 6. Effect of corrected shear rate on corrected viscosity of the composite of recycled HDPE with 25% recycled tire rubber particles at five different temperatures.

4.2 Effect of Shear Stress

Figure 7 exhibits effect of corrected shear stress on corrected viscosity of recycled HDPE at a temperature range between 160 and 250 °C. Viscosity became smaller when shear stress was elevated. As temperature rose from 160 to 250 °C, viscosity decreased at any shear stress. Figure 8 through Figure 12 depict relationship between corrected viscosity and corrected shear stress for composites of recycled HDPE with various content of rubber particles at different temperatures. For all the five composites, viscosity decreased as shear stress was increased. The higher concentration of recycled tire rubber particles, the higher the viscosity

The Ostwald-deWaele equation (Brysdon, 1981) can be used to explain the above pseudoplastic behavior. The equation takes the form of

$$\tau = K(\dot{\gamma})^n \qquad (13)$$

where τ is shear stress, $\dot{\gamma}$ shear rate, n flow index and K a adjustable parameter, which depends on the magnitude of n. According to viscosity definition:

$$\eta \equiv \frac{\tau}{\dot{\gamma}} \qquad (14)$$

Combining Eqs (13) and (14), viscosity can be express as follow:

$$\eta = \frac{K\dot{\gamma}^n}{\dot{\gamma}} = K(\dot{\gamma})^{(n-1)} \qquad (15)$$

Since previous results showed that increasing shear rate decreased viscosity n is less than 1. This fact further explains the composite is a pseudoplastic material.

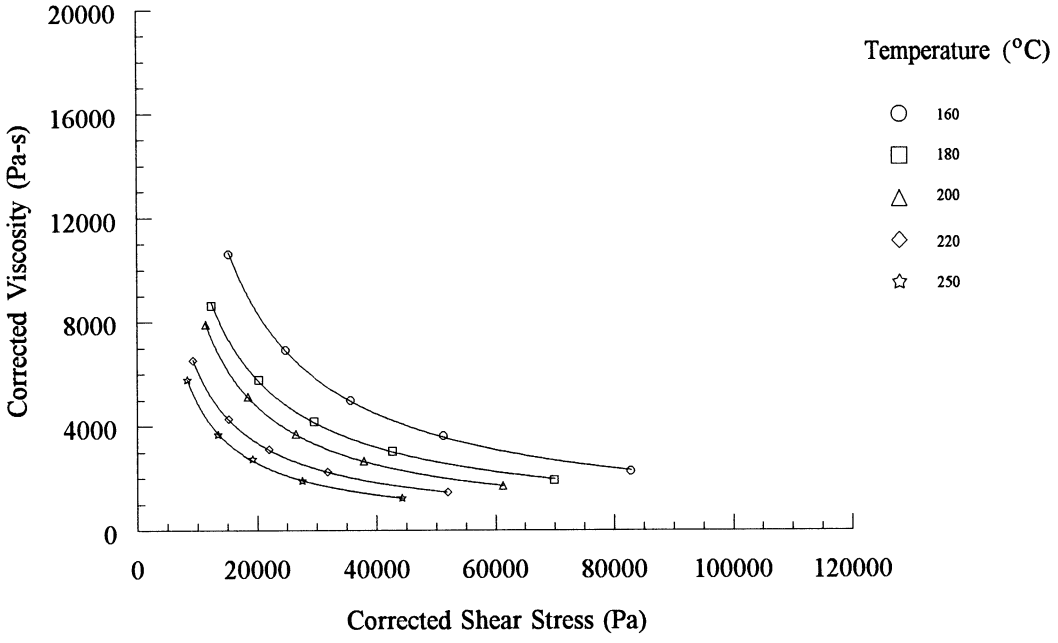

Figure 7. Effect of corrected shear stress on corrected viscosity of recycled HDPE.

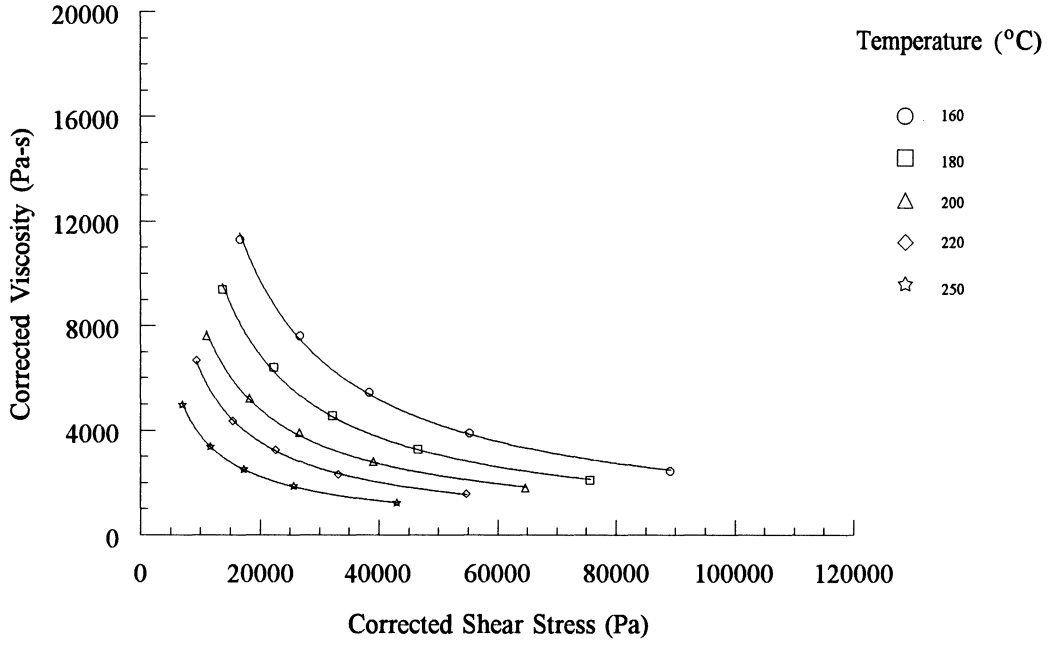

Figure 8. Effect of corrected shear stress on corrected viscosity of the composite of recycled HDPE with 5% recycled tire rubber particles at five different temperatures.

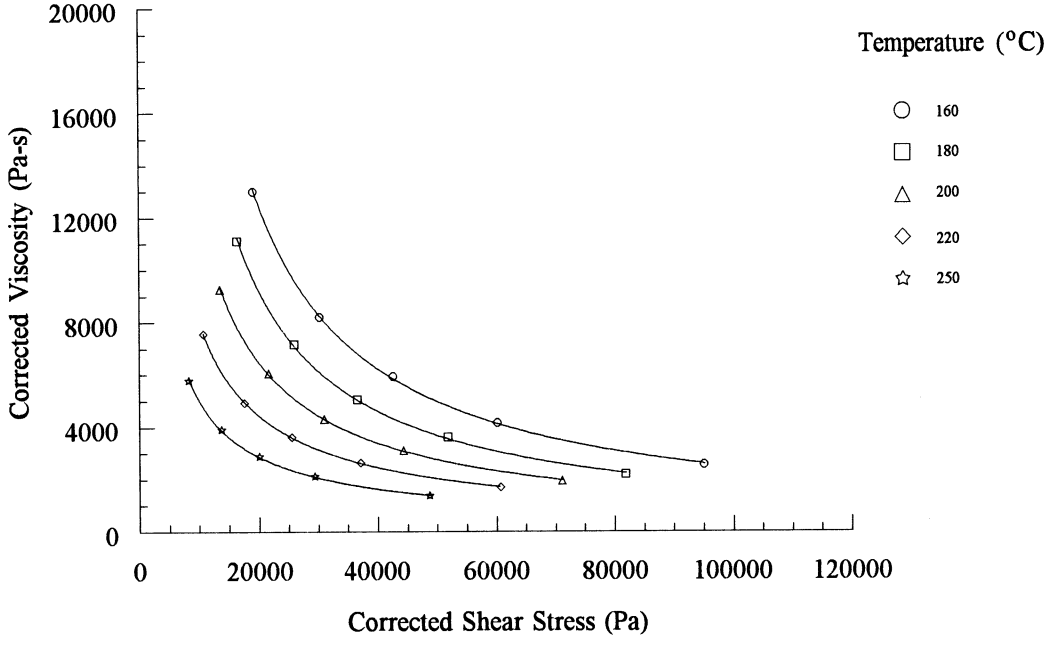

Figure 9. Effect of corrected shear stress on corrected viscosity of the composite of recycled HDPE with 10% recycled tire rubber particles at five different temperatures.

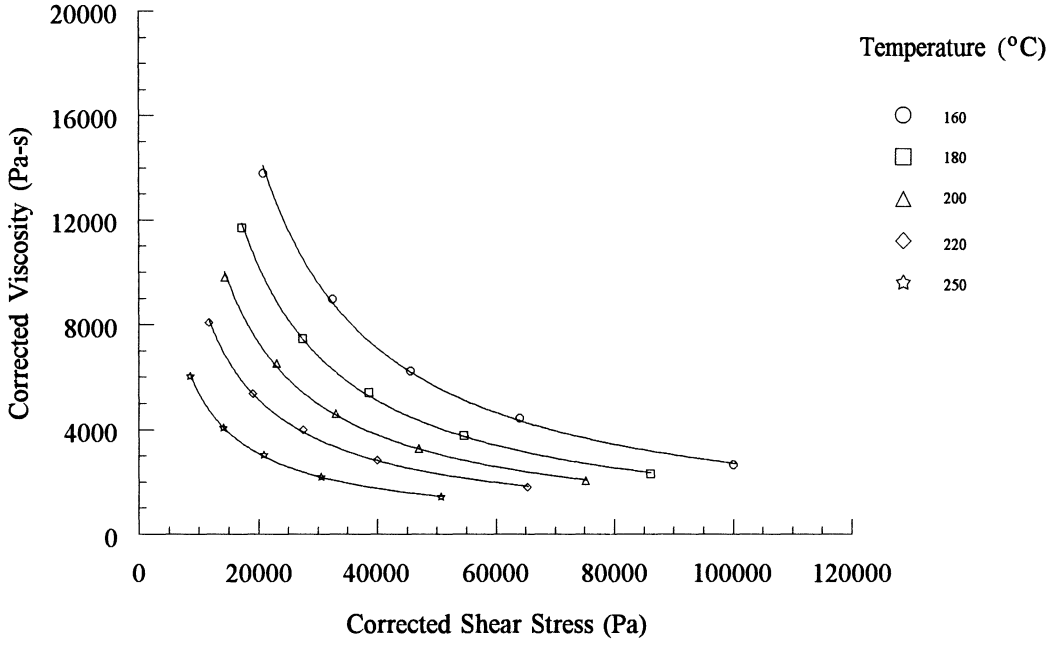

Figure 10. Effect of corrected shear stress on corrected viscosity of the composite of recycled HDPE with 15% recycled tire rubber particles at five different temperatures.

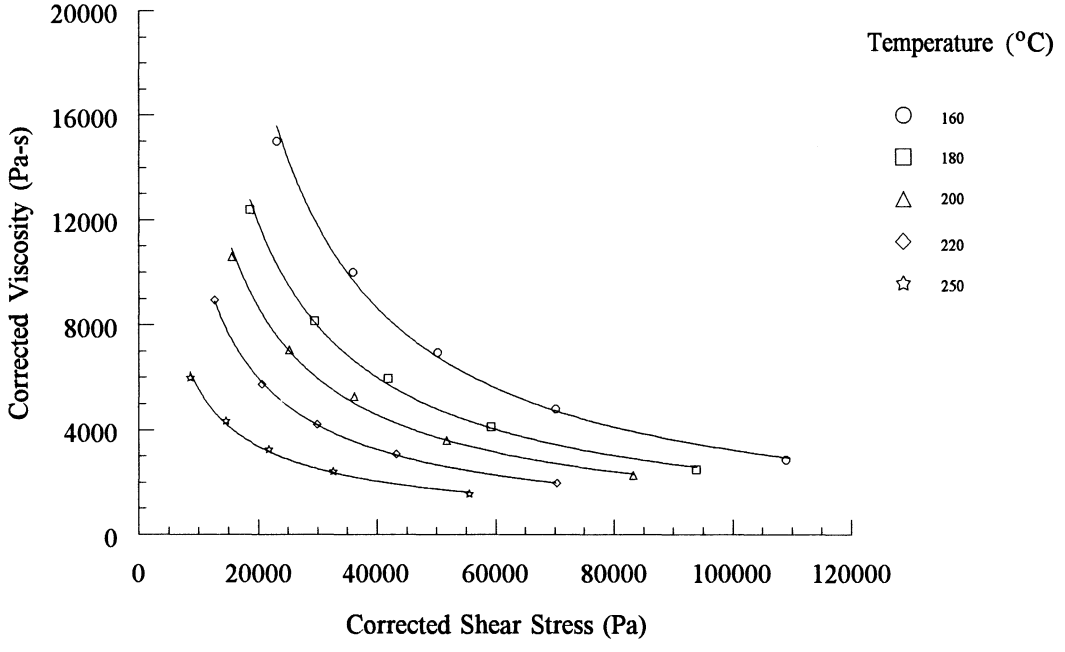

Figure 11. Effect of corrected shear stress on corrected viscosity of the composite of recycled HDPE with 20% recycled tire rubber particles at five different temperatures.

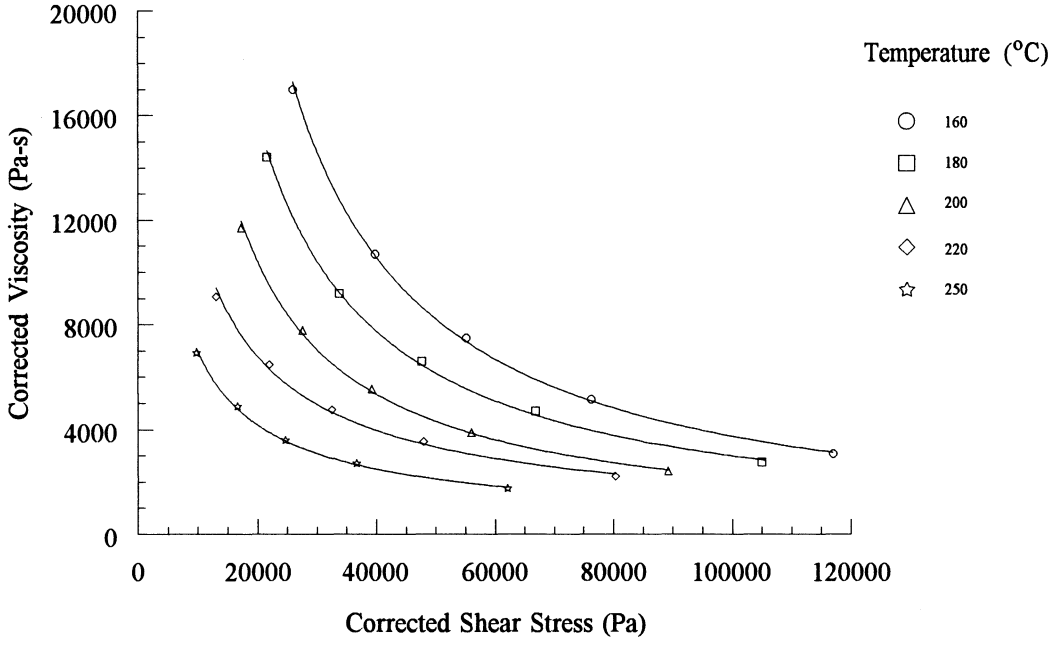

Figure 12. Effect of corrected shear stress on corrected viscosity of the composite of recycled HDPE with 25% recycled tire rubber particles at five different temperatures.

4.3 Effect of Temperature

Figure 13 displays the viscosity as a function of temperature for recycled HDPE at five different shear rates. Viscosity decreased when temperature rose. The rate of viscosity decrease with increasing temperature is more drastic at a lower shear rate.

The plots on Figures 14 to 18 present the variation of viscosity with temperature from 160 to 180 °C for composites of recycled HDPE with 5, 10, 25, 20 and 25% recycled rubber particles. For all the composites, viscosity decreased with increasing temperature. The rate of decrease in viscosity with increasing temperature is more drastic at lower shear rates. It is also noticed that the effect of shear rate on viscosity of the composites is more significant at a lower temperature than higher temperature.

The behavior can be explained qualitatively by the following relation (Brydson, 1981).

$$\frac{\eta}{\eta_g}) = -\frac{C^g{}_1(T-T_g)}{C^g{}_2+T-T_g} \qquad (15)$$

where η is viscosity, η_g viscosity at glass transition temperature, $C^g{}_1$ and $C^g{}_2$ constants, T_g glass transition temperature, T temperature. This equation can be rewritten as follow:

$$\log\eta=\log\eta_g - \frac{C^g{}_1(T-T_g)}{C^g{}_2+T-T_g} \qquad (16)$$

When temperature is increased, $\frac{C^g{}_1(T-T_g)}{C^g{}_2+T-T_g}$ will be increased, $\log\eta=\log\eta_g - \frac{C^g{}_1(T-T_g)}{C^g{}_2+T-T_g}$ will be smaller because log η_g is a constant. Therefore, viscosity will decrease when temperature increases.

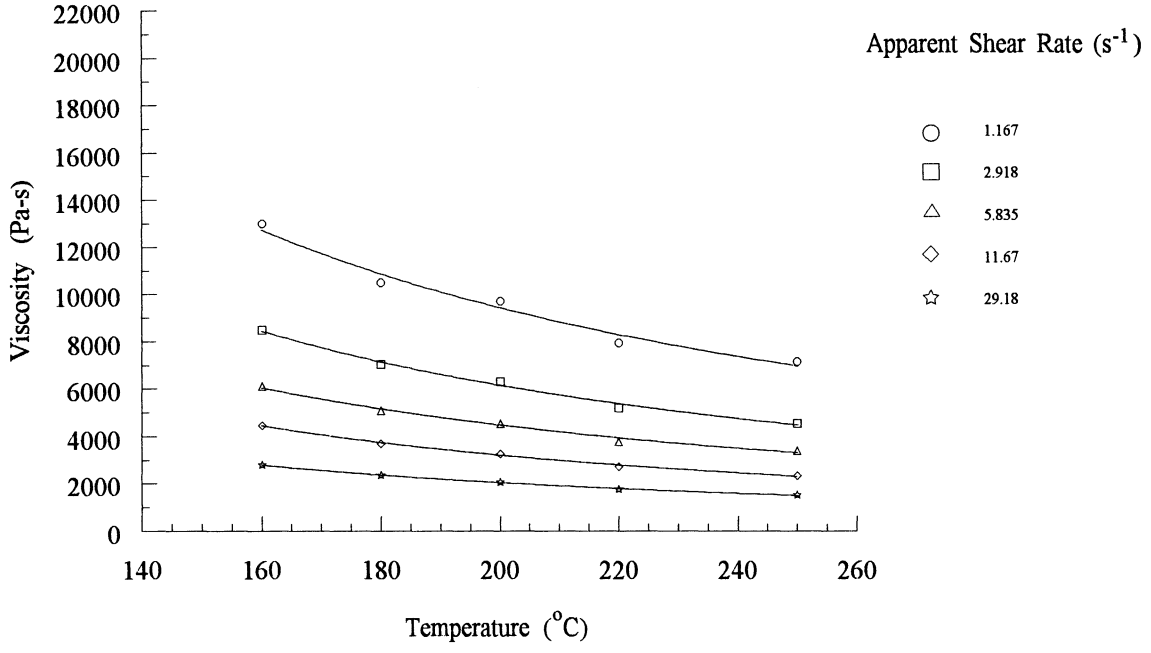

Figure 13. Viscosity as a function of temperature for recycled HDPE at five different shear rates.

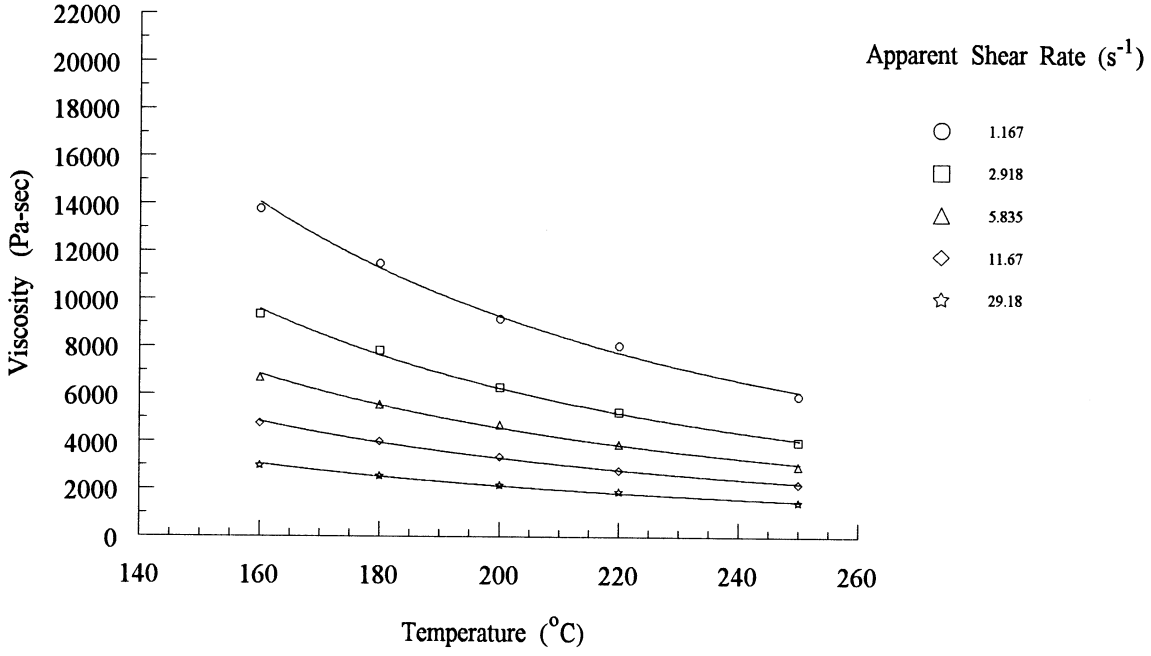

Figure 14. Viscosity as a function of temperature for the composite of recycled HDPE with 5% recycled tire rubber particles at five different shear rates.

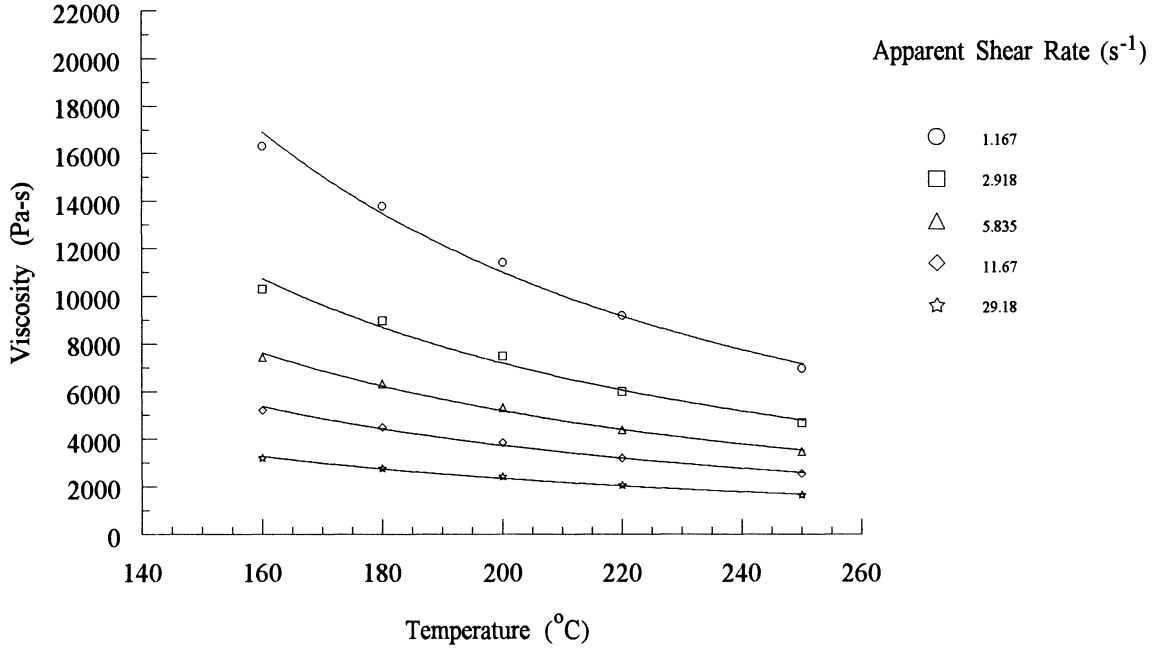

Figure 15. Viscosity as a function of temperature for the composite of recycled HDPE with 10% recycled tire rubber particles at five different shear rates.

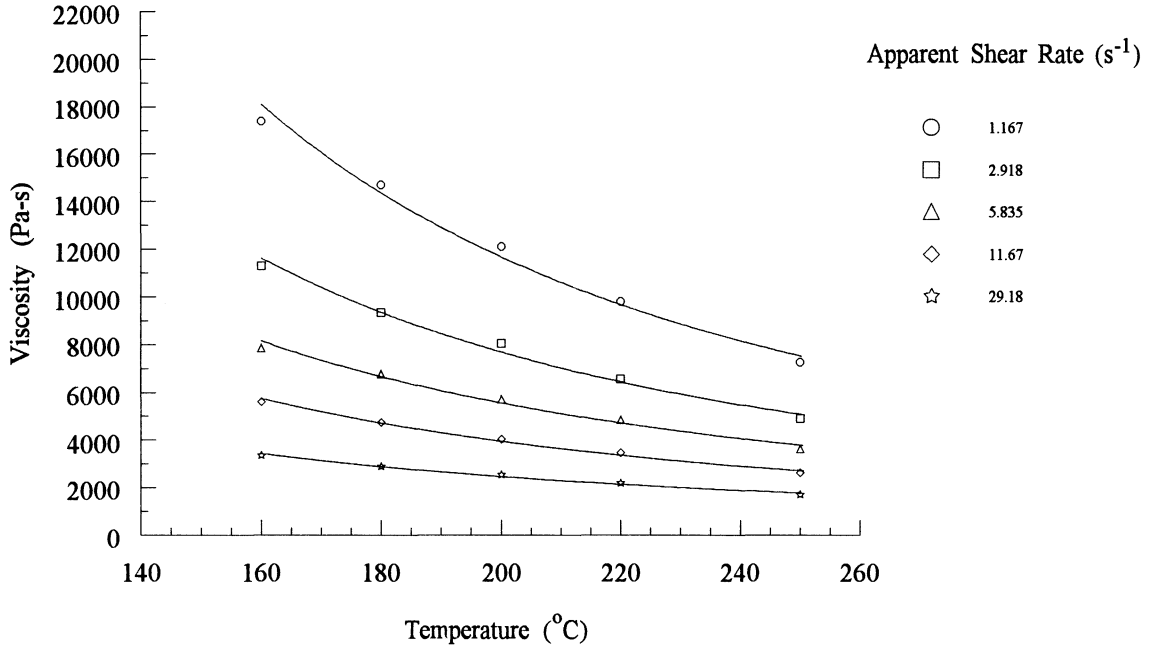

Figure 16. Viscosity as a function of temperature for the composite of recycled HDPE with 15% recycled tire rubber particles at five different shear rates.

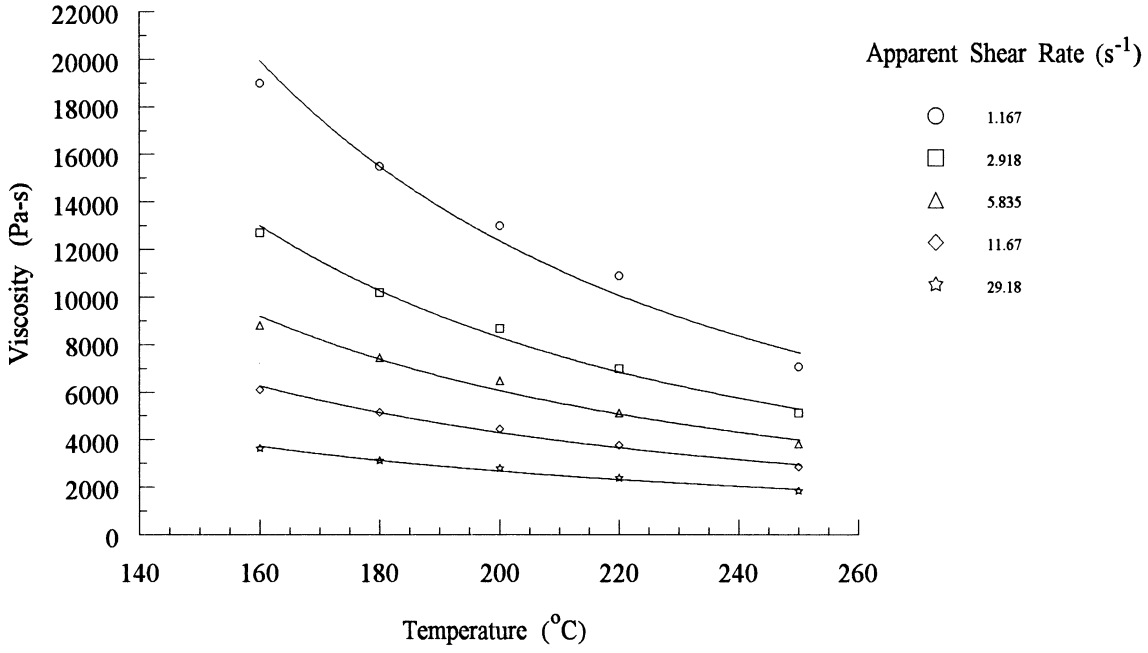

Figure 17. Viscosity as a function of temperature for the composite of recycled HDPE with 20% recycled tire rubber particles at five different shear rates.

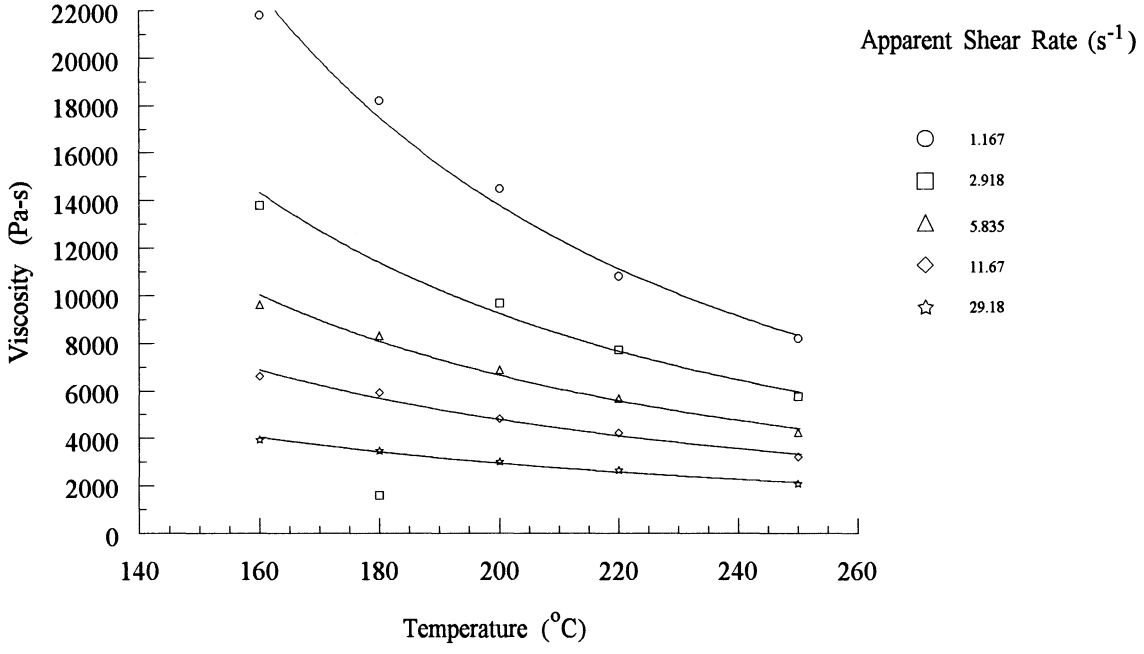

Figure 18. Viscosity as a function of temperature for the composite of recycled HDPE with 25% recycled tire rubber particles at five different shear rates.

4.4 Effect of Concentration of Recycled Tire Rubber Particles

Figures 19 through 23 show the variation of apparent viscosity of the composites with concentration of recycled tire rubber particles at a temperature of 160, 180, 200, 220 and 250 °C, respectively. At all the temperatures, the viscosity of the composites increased with increasing rubber concentration. The change in viscosity with concentration is more noticeable at a lower shear rate. Moreover, the change is more drastic at a lower temperature than at a higher temperature.

Results of the composites in Figures 19-23 could be explained in terms of crosslinked particles, which could be increased in recycled HDPE during the process of making composites. In addition, in the range of temperatures between 160 and 250 °C, crosslinking could happen between recycled HDPE and recycled tire rubber particles. Adding more recycled tire rubber led to more crosslinked particles and stronger crosslinking action in the composites. So the more recycled tire rubber particles in the composites, the higher viscosities they have.

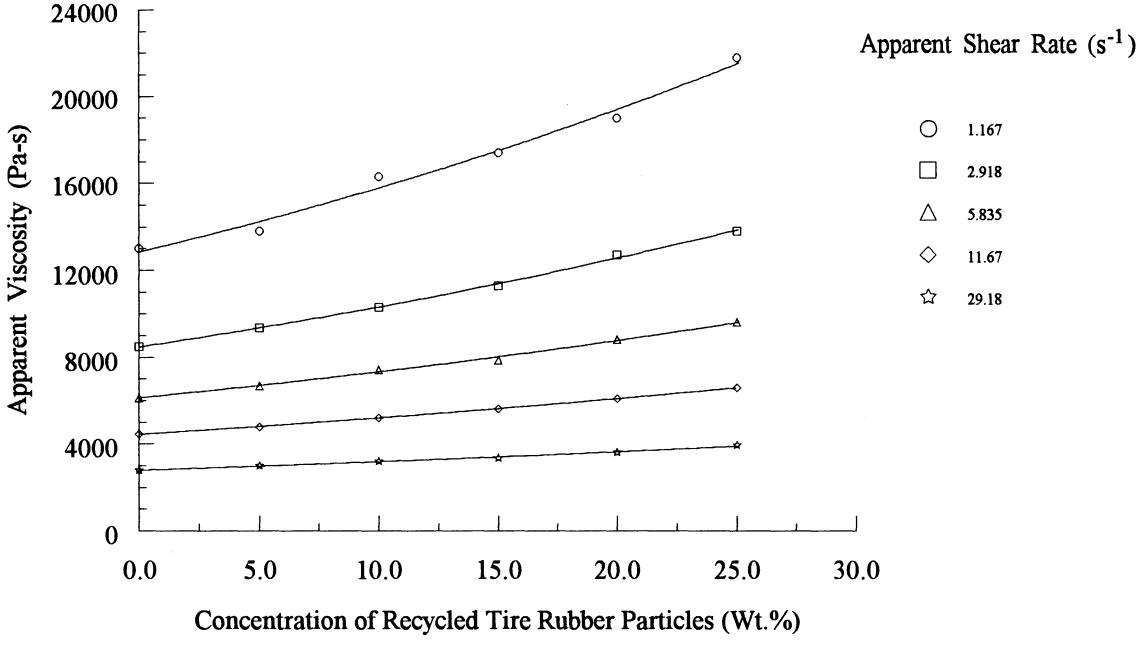

Figure 19. Apparent viscosity of composites as a function of concentration of recycled tire rubber particles at five different shear rates at 160 °C.

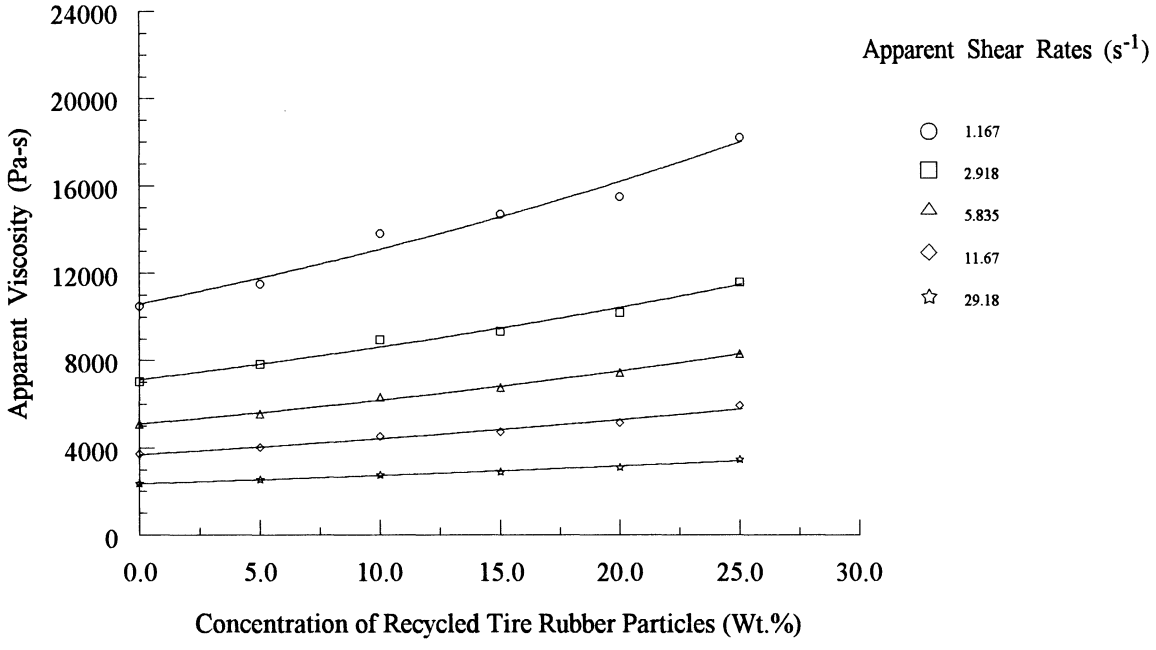

Figure 20. Apparent viscosity of composites as a function of concentration of recycled tire rubber particles at five different shear rates at 180 °C.

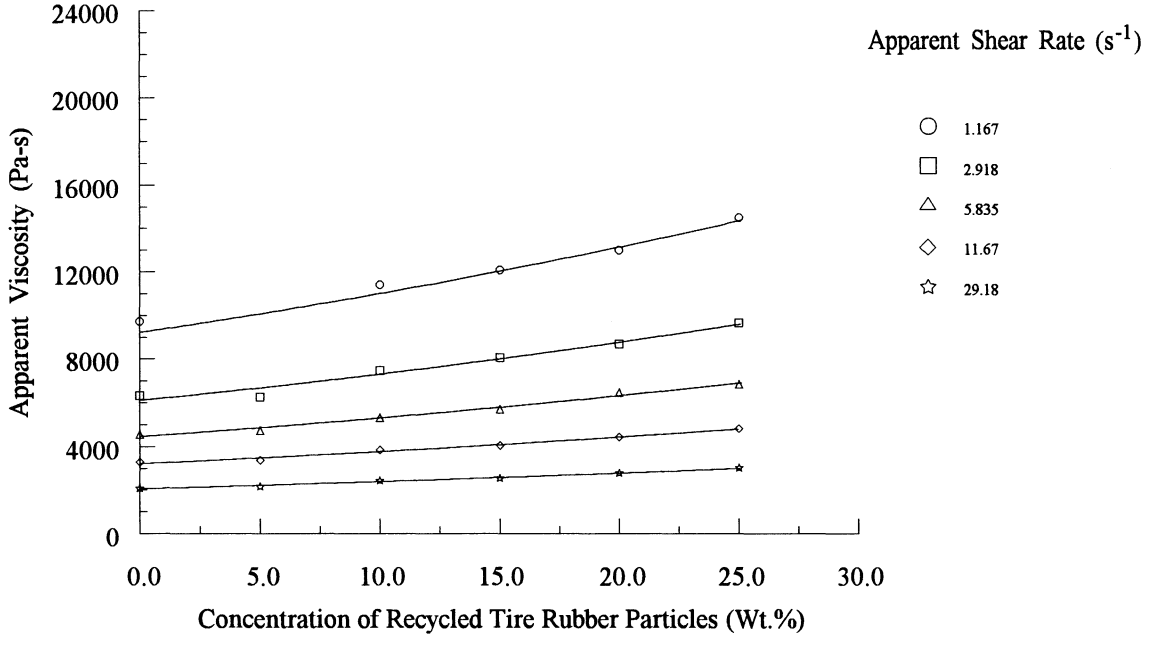

Figure 21. Apparent viscosity of composites as a function of concentration of recycled tire rubber particles at five different shear rates at 200 °C.

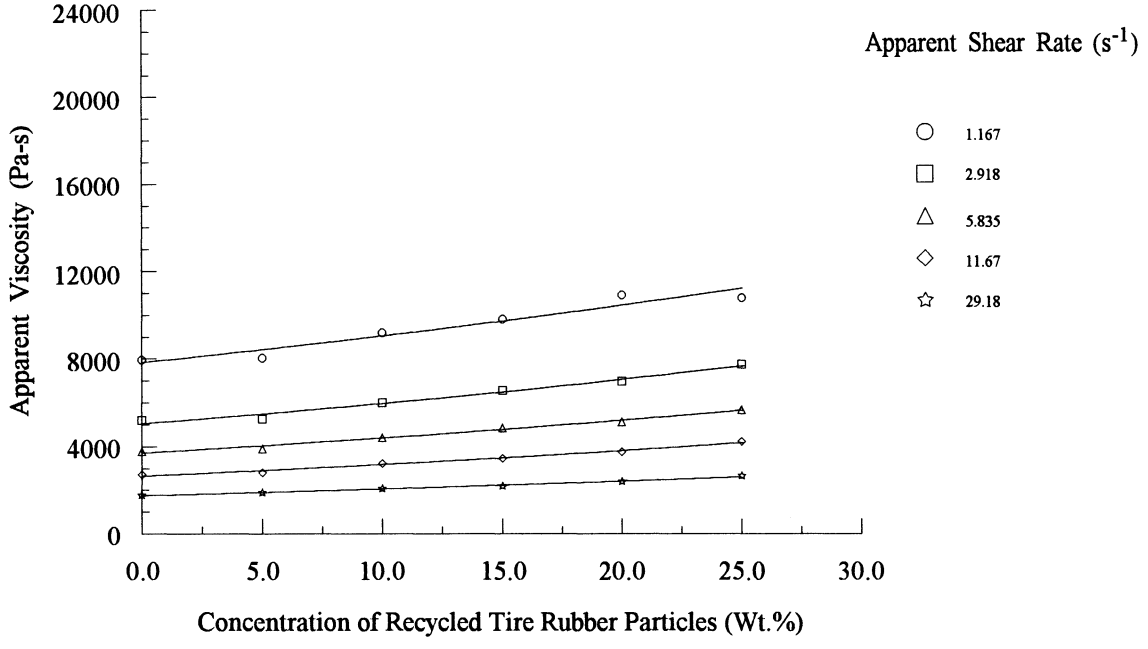

Figure 22. Apparent viscosity of composites as a function of concentration of recycled tire rubber particles at five different shear rates at 220 °C.

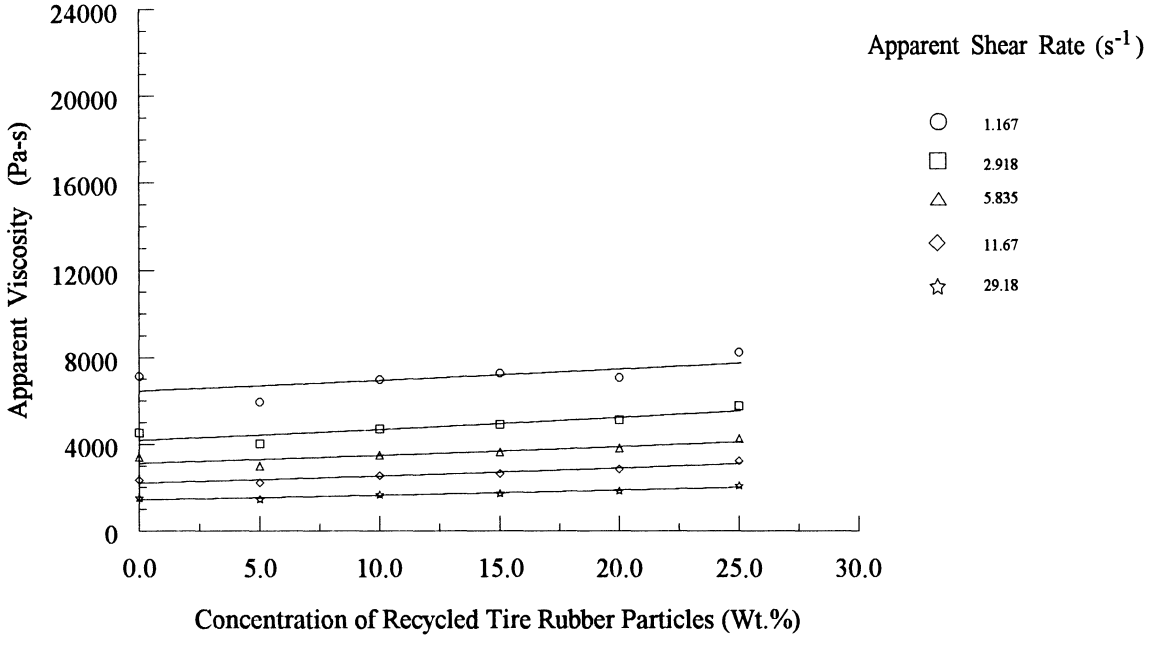

Figure 23. Apparent viscosity of composites as a function of concentration of recycled tire rubber particles at five different shear rates at 250 °C.

4.5 Effect of Heating Duration

Figure 24 displays the viscosity of recycled HDPE as a function heating time at 220 °C and various shear rates. The heating time was used to simulate the actual heat history a polymer may experience due to repeated recycling. Within the heating time up to 240 mined, there was little change in the viscosity of recycled HDPE. For a polymer, viscosity is related to its molecular structure. Thus, it is believed that the molecular structure of recycled HDPE is not significantly degraded due to extended heating.

Figures 25 through 29 present viscosity as a function of heating duration for the composites of recycled HDPE with recycled tire rubber particles of 5, 10, 15, 20 and 25%. It is noted that the rheological behavior of the composites was relatively stable with increased heating duration. This fact suggests that the structure of the composite system is fairly stable over the heating duration.

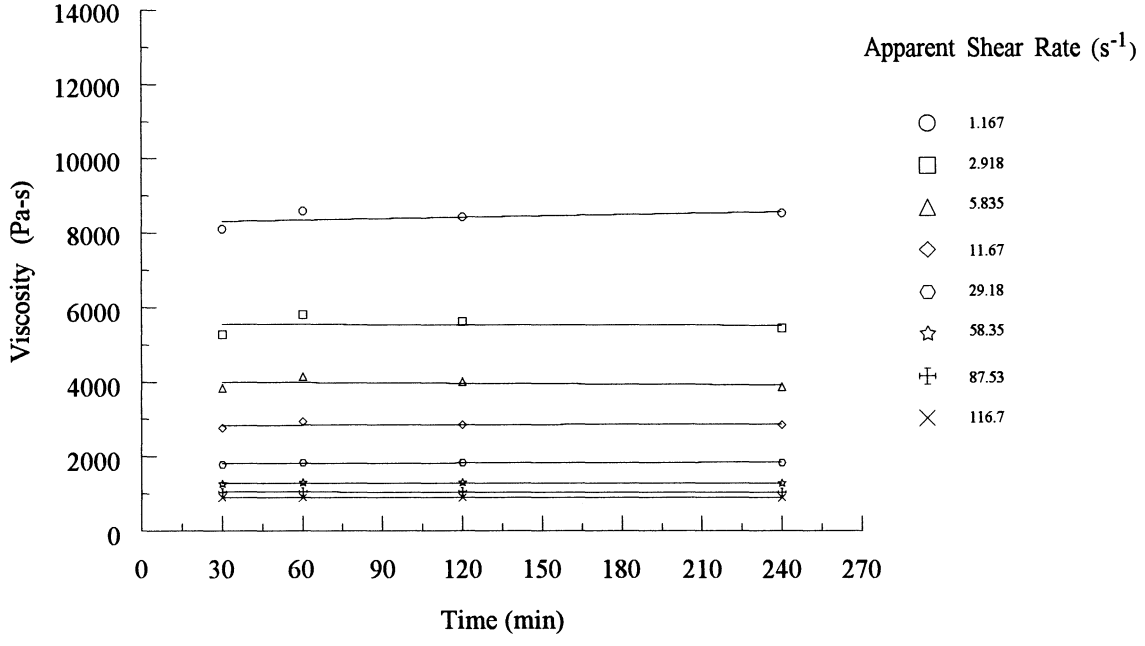

Figure 24. Viscosity of recycled HDPE as a function of heating duration at various shear rates.

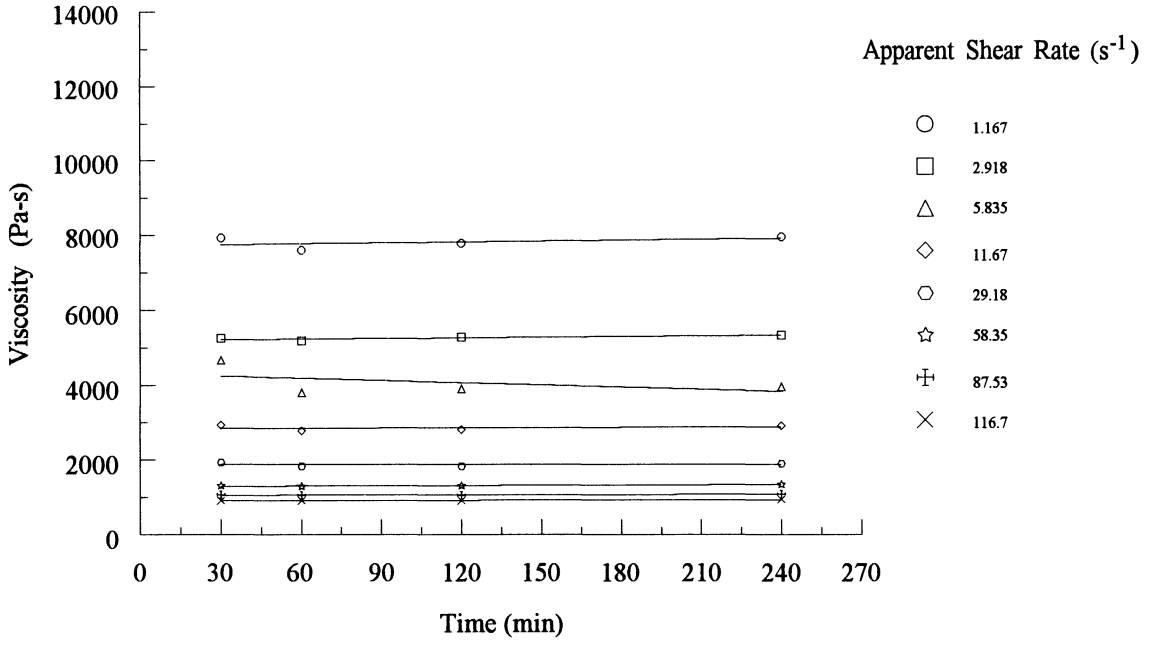

Figure 25. Viscosity of the composite of recycled HDPE with 5% recycled tire rubber particles as a function of heating duration at various shear rates.

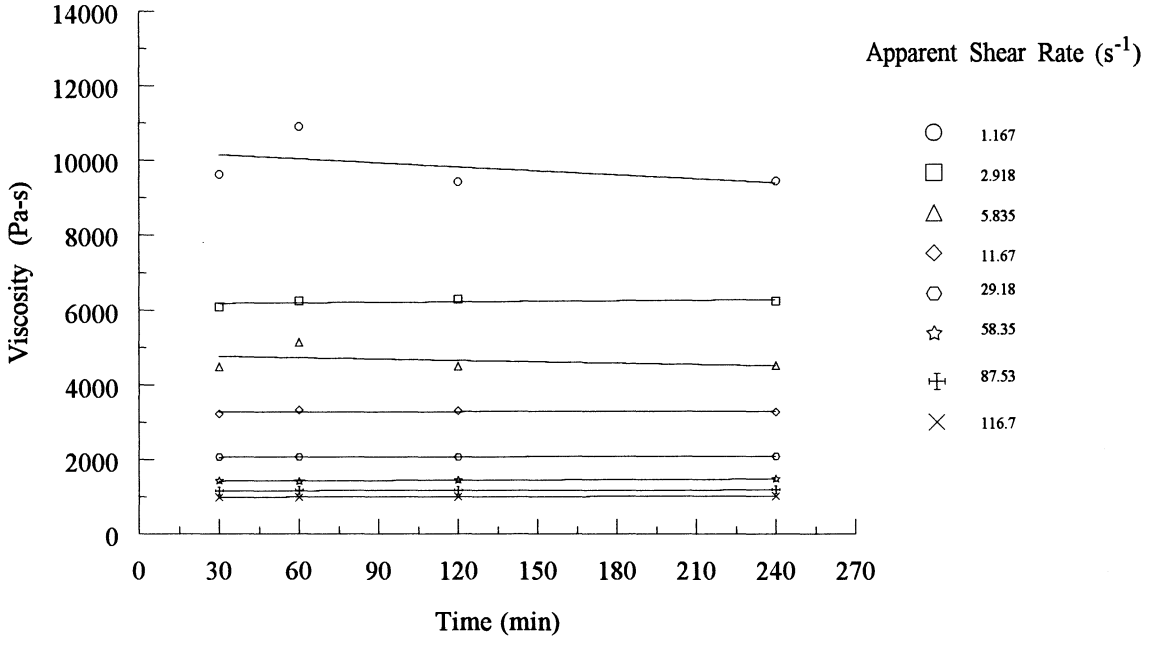

Figure 26. Viscosity of the composite of recycled HDPE with 10% recycled tire rubber particles as a function of heating duration at various shear rates.

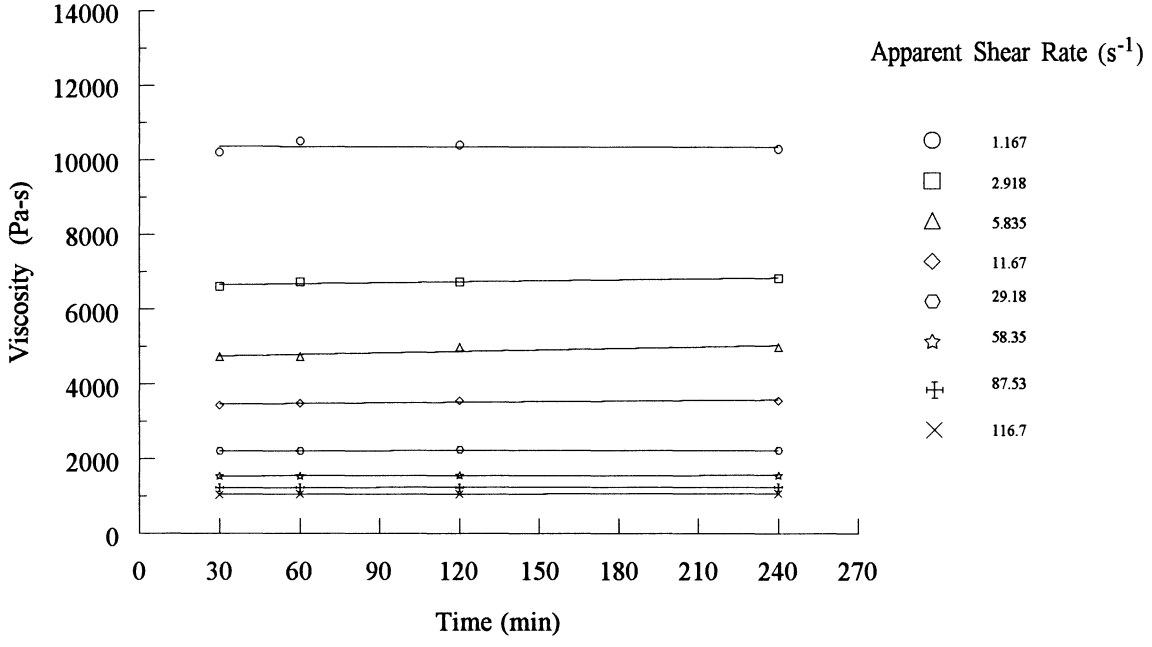

Figure 27. Viscosity of the composite of recycled HDPE with 15% recycled tire rubber particles as a function of heating duration at various shear rates.

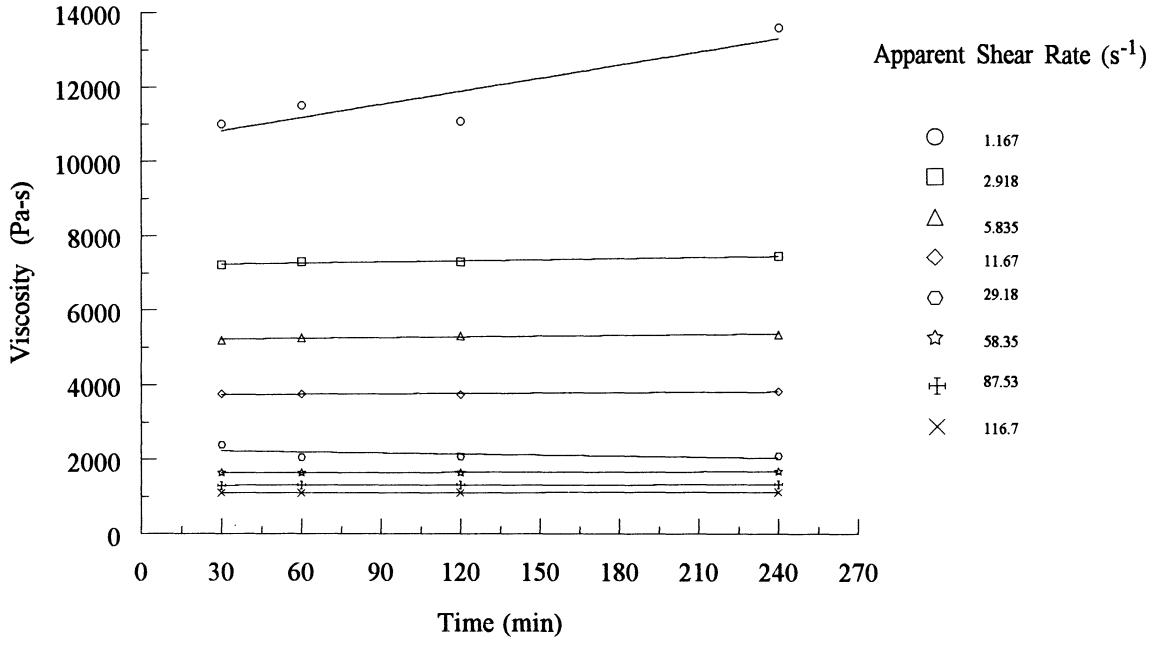

Figure 28. Viscosity of the composite of recycled HDPE with 20% recycled tire rubber particles as a function of heating duration at various shear rates.

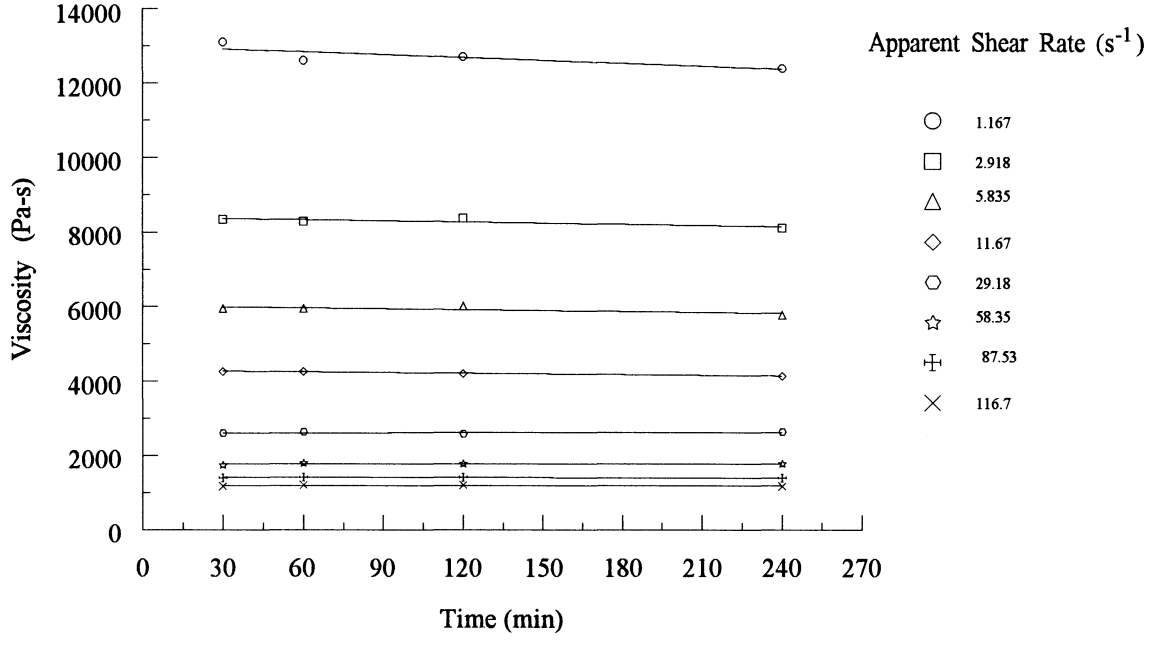

Figure 29. Viscosity of the composite of recycled HDPE with 25% recycled tire rubber particles as a function of heating duration at various shear rates.

CHAPTER 5

Conclusions

The following conclusions were made according to the study on the rheological behavior of composite of recycled HDPE with recycled tire rubber particles.

1. The composites were pseudoplastic materials, *i.e.*, the viscosity decreased when either shear rate or shear stress increased.

2. When corrected shear rate is smaller than 7.5 s^{-1}, viscosity of the composites declined sharply with increasing shear rate.

3. The viscosity of the composites decreased with the elevation of temperature.

4. Viscosity increased with increasing concentration of recycled tire rubber particles.

5. After being heated up to 240 mined at 220 °C., recycled HDPE and the composites of recycled HDPE with recycled rubber particles did not show a significant change in viscosity.

CHAPTER 6

Recommendations for Further Study

The following recommendations for further study were made:

1. To relate rheological characterization study to practical production and make the product design and output in a more efficient and economic way, higher shear rates should be studied because products are produced at higher shear rate in commercial processing operations.

2. There will be more practical meaning to investigate viscosities of the composites under different temperatures at given heating duration. Thus, manufacturers could choose better operating parameters for the process of the composites, which minimizes the material degradation at higher temperature during processing.

3. It will be better to investigate effect of particles size of recycled tire rubber on viscosity of composites.

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